14

LIGHT SCATTERING IN CELLULOSE ACETATE SOLUTIONS*

N. K. SUBRAMANIAN

DEPARTMENT OF PHYSICS, INDIAN INSTITUTE OF SCIENCE, BANGALORE 12

AND

S. R. SIVARAJAN

AHMEDABAD TEXTILE INDUSTRY'S RESEARCH ASSOCIATION, AHMEDABAD

(*Received, December* 20, 1960)

ABSTRACT. A detailed investigation of the light scattered by solutions of blank and dyed samples of cellulose acetate in acetone has been carried out. The method developed by Horn *et al.* has been employed for the estimation of molecular length L of the cellulose acetate molecules from the observed depolarisation factor ρ_v and the angular distribution of intensity. In a solution of dyed samples the dye molecules cause a shielding between the dyed molecules, thus producing a decrease in intermolecular interaction. Dyeing in general causes a straightening of the wave-like form of the cellulose acetate molecules thus producing an increase in molecular length. In this respect surface dyeing is less effective than either the interior dyeing or full penetration. The dispersion of depolarisation ρ_v and dissymmetry Z of the scattered light from these samples have also been discussed from considerations of intermolecular and intramolecular interactions.

INTRODUCTION

Light scattering studies on solutions of cellulose acetate in acetone were carried out for the first time by Doty and Kaufman (1945). A more extensive study on cellulose acetate was made by Stein and Doty (1946). They determined the particle size, shape and molecular weight of cellulose acetate in acetone and established that the smaller molecules were fully extended in solution i.e., the molecules were more or less rod-like, but the larger ones were built up in the form of gentle waves.

The present work on the scattering of light in cellulose acetate solutions was undertaken in order to study the effect of dyeing on cellulose acetate. Here the cellulose acetate molecules will be assumed to be rod-like after Stein and Doty (1946) because the theory of light scattering has been thoroughly dealt with for rod-shaped particles.

* Communicated by Prof. R. S. Krishnan.

2. PREPARATION OF SAMPLES

The cellulose acetate used here is a secondary cellulose acetate staple fibre soluble in acetone and only about 2.5 groups on an average are acetylated. For practical purposes this has been taken as blank cellulose acetate fibre.

The dyed samples of cellulose acetate were prepared in the following manner. The samples were deposited by double decomposition technique for $PbCrO_4$, PbI_2 and Ag. The washed and boiled fibres were immersed in saturated lead acetate solution for a few hours, the excess liquid was squeezed out and then the fibre was immersed for a few hours in 5% $K_2Cr_2O_7$ for getting $PbCrO_4$ deposits. fibre+PbAc$\Longrightarrow$PbAc+fibre+$K_2Cr_2O_7\Longrightarrow$$PbCrO_4$ on fibre KAc etc. The fibre was immersed in polyiodide solution for PbI_2 deposits. For Ag deposits, the fibres were immersed in $AgNO_3$ solution for a few hours and the excess $AgNO_3$ solution was squeezed out. The fibres were then immersed in boiling 3% glucose solution, whereby reduction of Ag was completed. Fibres were all finally thoroughly washed, soaped and boiled in water, dried and combed out to remove loosely adhering particles.

Three types of dyeing were employed.

(a) *Fully penetrated*: This was accomplished by prolonged soaking of the fibres (1 week) in each of the solutions used.

(b) *Interior dyed*: These samples were obtained by stripping of from the fibre surface the deposits formed there using dilute acid for 15-25 seconds.

(c) *Surface dyed*: These were obtained by immersion in each of the solutions used for 15-30 minutes.

The dye deposits in the surface dyed samples are in the grooves of the surface only. Interior dyed fibres contain deposits only in the channels inside the fibre, while the fully penetrated dyed fibres are interior and surface dyed.

The eleven samples obtained are the following :—

1	Blank cellulose acetate			
2	$PbCrO_4$	on	cellulose acetate	(fully penetrated)
3	,,	,,	,,	(surface dyed)
4	,,	,,	,,	(interior dyed)
5	PbI_2	,,	,,	(fully penetrated)
6	,,	,,	,,	(surface dyed)
7	,,	,,	,,	(interior dyed)
8	Ag	,,	,,	(fully penetrated) dev with H_2O_2
9	,,	,,	,,	(surface dyed)
10	Ag	,,	,,	(fully penetrated) dev with glucose
11	,,	,,	,,	(surface dyed)

10 mgs of each sample was carefully weighed and dissolved in 100 ml of double distilled analar acetone. This was taken as the parent solution. Its concentration was obviously 0·01 gm/ml. The lower concentrations of the samples were then prepared by diluting the parent solution adding known volumes of the solvent. In this manner for each sample, four different solutions with concentrations (0·01, 0·005, 0·0025 and 0·00125 gm/100 cc) were prepared.

These samples were prepared at the chemical laboratories of ATIRA and the physical measurements were carried out at the Physics Department of the Indian Institute of Science.

3. EXPERIMENTAL DETAILS

The measurements of the intensity of scattering were carried out with a photoelectric photometer constructed here. The optical arrangement is of the conventional type. A RCA 931-A photomultiplier tube served as a detector A cathode follower amplifier was used to amplify the current from the PM. A balanced arrangement was employed to minimise the drift voltages. The amplified output was read on a microammeter or on a sensitive galvanometer when more accuracy was required. The readings obtained with this instrument were found to be quite reliable. This was checked by comparison with a Brice-Phoenix instrument.

Provision was made for interposing polaroids in the incident and scattered sides for getting vertically and horizontally polarised components. The sensitivities of the photomultiplier set up for vertically and horizontally polarised light were measured and the differences were found to be usually less than two per cent. Necessary corrections were made in the readings taken with the instrument while working with cellulose acetate solution.

The sample to be studied was kept in a cylindrical glass vessel which was provided with flattened openings for entrance and exit of the incident beam. Measurements of the angular distribution of the intensities of the three components V_v, V_h and H_h of the scattered light were carried out for the following values of the scattering angle θ; 45°, 55°, 65°, 75°, 90°, 105°, 115° and 125° from the forward direction. For each sample the angular distribution of the intensity of scattered light were measured for three different wavelengths, namely, 4358 Å, 5461 Å, 5790 Å and for four different concentrations. All the readings were converted to the same arbitrary unit. These values were corrected for effective volume by multiplying them by the corresponding value of $\sin\theta$.

4. RESULTS

Table I gives the corrected values of intensity of scattering for various angles for the three components for one typical case, namely, $PbCrO_4$ on cellulose acetate (interior dyed) of concentration 0·005 gm/100 cc at 5461 Å.

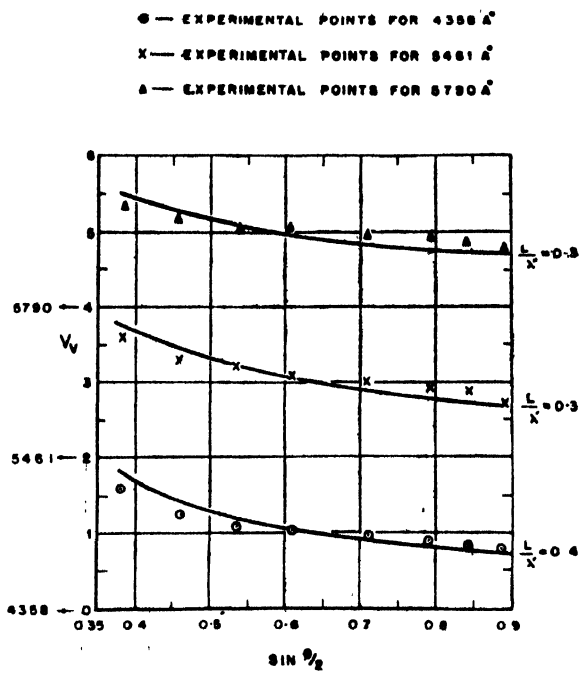

Fig. 3. Variation of V_v with sin $\theta/2$.

TABLE II

Particle length

No.	Samples	Length A.U.
1.	Blank celluloso acetate	560
2.	$PbCrO_4$ (F. Penetrated)	430
3.	$PbCrO_4$ (S. Dyed)	960
4.	$PbCrO_4$ (I. Dyed)	1280
5.	PbI_2 (F. Penetrated)	980
6.	PbI_2 (S. Dyed)	640
7.	PbI_2 (I. Dyed)	1040
8.	Ag (F. Penetrated) dev. H_2O_2	1165
9.	Ag (S. Dyed)	900
10.	Ag (F. Penetrated) dev. glucose	1200
11.	Ag (S. Dyed)	1160

taking the total intensity of the components i.e., $(V_v+2V_h+H_h)$ for each angle. Typical results obtained with eleven samples for one concentration, namely 0·005 gm/100 cc., are given in Table III.

TABLE III

Samples No.	Dimensions AU	Depolarisation ρ_v%, 4358Å	5461Å	5790Å	dissymmetry Z, 4358Å	5461Å	5790Å	Total intensity at 90° for 5461Å zero concn.
1	560	9.8	5.5	7.0	4.08	5.17	3.59	190
2	430	6.5	6.1	6.4	3.90	4.94	3.45	90
3	960	25.0	21.6	24.4	2.54	3.18	2.35	155
4	1280	24.0	19.6	24.0	1.83	2.42	1.60	180
5	980	33.3	30.6	26.4	1.96	2.46	1.80	185
6	640	8.7	9.5	8.5	2.80	3.69	2.80	120
7	1040	25.0	23.0	27.0	2.69	3.01	2.43	130
8	1165	29.0	30.3	29.0	2.15	2.80	2.09	150
9	900	11.6	9.3	11.2	2.69	3.37	2.56	130
10	1200	28.9	27.3	26.0	1.93	2.76	1.95	190
11	1160	34.7	28.7	31.2	2.13	2.90	2.08	170

5. DISCUSSION

It is well known that the dissymmetry of scattering arises from interferences due to interaction of waves scattered by different parts of the molecule (intramolecular) and also due to the interaction between the waves originating from different molecules (intermolecular).

The dependence of dissymmetry on concentration assuming the hard sphere model has been given in an approximate form by Oster (1949) and Doty *et al.* (1951). This can be written as $Z = Z_0\left(1 - \frac{Kc}{\lambda^2}\right)$ where Z_0 is the dissymmetry at zero concentration. This equation can be extended to the case of rods.

From the above equation it is evident that the presence of intermolecular effect is to increase the dissymmetry with wavelength and is proportional to $\left(1 - \frac{K}{\lambda^2}\right)$ Mommaerts (1951, 1957), Oster (1948, 1949). The presence of intramolecular effect is to decrease the dissymmetry as the wavelength increases and is proportional to $1/\lambda$ (Horn, *et al.*, 1951). At finite concentration these two effects will contribute to the total dissymmetry and hence the dispersion of dissymmetry may not be linear. This has been observed experimentally.

It is seen from the figure of dissymmetry against L/λ' for various values of δ (Horn 1955) that for one value of Z, δ increases as L/λ' increases, i.e., δ in-

creases as λ decreases at infinite dilution. But $\rho_v = 3\delta^2/5+4\delta^2$. Therefore ρ_v increases as λ decreases. From the same figure we also note that for any one value of L/λ' dissymmetry increases as ρ_v decreases. Thus the variation of depolarisation factor ρ_v with wavelength is opposite to the variation with wavelength of dissymmetry.

In Table II are given the estimated values of the molecular length of eleven cellulose acetate samples. It is seen that the lengths of the dyed samples are in general greater than that of blank cellulose acetate sample. This increase in length of the dyed samples can be explained as a straightening of wavelike form of cellulose acetate chain as the dye penetrates into its pores. The lengths of the cellulose acetate molecules in fully penetrated sample and interior dyed sample are nearly the same but greater than that in surface dyed samples. In the case of sample 2, vide Table II, the micellar length comes out to be smaller than the corresponding values of the other samples. The depolarisation factor ρ_v is also the lowest for this sample. In the process of preparing the fully penetrated dyed sample, the micelles appear to have broken into smaller sizes.

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to Professor R. S. Krishnan for guidance and encouragement. Thanks are also due to Dr. P. S. Narayanan and Mr. S. Subramanian for valuable discussions.

REFERENCES

Doty *et al.*, 1951, *Adv. Prot. Chem.*, **6**, 37.
Doty, P. and Kaufman, H. S., 1945, *J. Phys. Chem.*, **49**, 583.
Horn, P., Thesis, Strasbourg, 1955.
Horn, *et al.*, 1951, *J. Chim. Phys.*, **48**, 530.
Mommaerts, W. F. H. M., 1951, *J. Biol. Chem.*, **188**, 553.
Mommaerts, *et al.*, 1957, *J. Biol. Chem.*, **224**, 277 .
Oster, G., 1948, *Chem. Rev.*, **43**, 309.
Oster, G., 1949, *Rec. Trav. Pays. Bas.*, **68**. 1123.
Stein, R. S. and Doty, P., 1946, *J. Am. Chem. Soc.*, **68**, 159.